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(71) Applicant: JAPAN SYNTHETIC RUBBER CO., LTD.
11-24, Tsukiji-2-chome Chuo-ku
Tokyo(JP)

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(72) Inventor: Matsumura, Yoshio
14-30, Tsukimino-8-chome
Yamato-shi(JP)

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(72) Inventor: Nozue, Ikuo
29, Aobadai-2-chome
Midori-ku, Yokohama(JP)

(72) Inventor: Ukachi, Takashi
29, Aobadai-2-chome
Midori-ku, Yokohama(JP)

(74) Representative: Beetz, sen., Richard, Dipl.-Ing.
Patentanwälte Dipl.-Ing. R. Beetz sen. Dipl.-Ing. K.
Lamprecht; Dr. Ing. R. Beetz jr. et al.,
Rechtsanwalt Dipl.-Phys. Dr. jur. U. Heidrich Dr.-Ing. W.
Timpe; Dipl.-Ing. J. Siegfried Dipl.-Chem. Dr.rer.nat.W.
Schmitt-Fumian Steinsdorfstrasse 10
D-8000 München 22(DE)

(54) Doped acetylene polymer and process for production thereof.

(57) Doped acetylene polymers are produced by immersing an acetylene polymer under an inert gas atmosphere in an organic solvent solution of a dopant selected from the group consisting of a platinum group metal complex, a carbonium salt, an oxonium salt and a parabenoquinone derivative. According to this process, a doped acetylene polymer having any desired electrical conductivity can be produced and the doped acetylene polymer thus obtained has excellent properties as an organic semiconductor material for solar batteries, various sensors, etc.

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DOPED ACETYLENE POLYMER AND
PROCESS FOR PRODUCTION THEREOF

1 This invention relates to a process for
producing a doped acetylene polymer. More particularly,
this invention relates to a process for the production
of an acetylene polymer doped with a specific dopant
5 selected from the group consisting of a platinum group
metal complex, a carbonium salt, an oxonium salt and
a parabenoquinone derivative.

Acetylene polymers are an insulator or semi-conductor having an electrical conductivity in the
10 order of $10^{-5} \Omega^{-1} \cdot \text{cm}^{-1}$ to $10^{-9} \Omega^{-1} \cdot \text{cm}^{-1}$ [See Macromol. Chem. Vol. 175, p. 1565 (1978)]. Heretofore, several methods have been proposed to improve the electrical conductivity of this polymer. For instance, J. Amer. Chem. Soc. Vol. 100, p. 1013 (1978) discloses a process
15 for increasing the electrical conductivity of an acetylene polymer by doping the acetylene polymer in the form of a film with HBr, Cl₂, Br₂, I₂, ICl, IBr, AsF₅, Na or the like as a dopant. The most effective dopants among them are I₂, AsF₅, etc., and the highest electrical conductivity obtained by this method is in the order of 10^2 $\Omega^{-1} \cdot \text{cm}^{-1}$. A process for doping with a silver salt such as AgBF₄ or AgClO₄, or FSO₂OOSO₂F has been proposed, respectively, on page 489 or 1066 of J. Chem. Soc. Chem. Comm. (1978). In the former case an electrical
25 conductivity in the order of $10^0 \Omega^{-1} \cdot \text{cm}^{-1}$ can be attained,

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1 and in the latter case, an electrical conductivity in
the order of $10^2 \Omega^{-1} \cdot \text{cm}^{-1}$ can be obtained. The doping
with these chemicals is carried out by allowing the
chemicals in the gaseous state or in the form of a
5 solution in a solvent to permeate the acetylene polymer,
because the acetylene polymer is insoluble in the
chemicals.

The present inventors have made an intensive
survey of a process for doping an acetylene polymer and
10 have consequently found that the acetylene polymer can
be doped with a platinum group metal complex, a
carbonium salt, an oxonium salt or a parabenoquinone
derivative.

An object of this invention is to provide a
15 novel doped acetylene polymer.

Another object of this invention is to provide
a novel process for producing the novel doped acetylene
polymer.

Other objects and advantages of this invention
20 will become apparent from the following description.

According to this invention, there is provided
an acetylene polymer doped with a platinum group metal
complex, a carbonium salt, an oxonium salt, or a
parabenoquinone derivative.

25 The doped acetylene polymer of this invention
can be prepared by immersing an acetylene polymer under
an inert gas atmosphere in an organic solvent solution
of the platinum group metal complex, carbonium salt,

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1 oxonium salt or parabenoquinone derivative.

The process of this invention has the following characteristic advantages, and in view of these advantages, this invention is wide in application field
5 and very valuable from the commercial point of view:

1. The dopant used in this invention is free from corrosiveness and volatility. This is very advantageous for the doping operation, and in addition, the doped acetylene polymer obtained is stable in performance.
10 2. According to the process of this invention, the electrical conductivity of the objective doped acetylene polymer can be regulated to any desired order of value.
3. The doped acetylene compound obtained by the
15 process of this invention has excellent performance as an organic semiconductor for solar batteries and various sensors.
4. In particular, the acetylene polymer doped with the platinum group metal complex, the carbonium salt or
20 the oxonium salt is excellent in heat-resistance and light-stability under an inert atmosphere or under vacuum.

The platinum group metal complex used in this invention is a platinum group metal complex active for
25 substitution reaction with olefines, and includes, for example, $(PhCN)_2PdCl_2$, $(COD)PdCl_2$, $[(C_2H_4)PdCl_2]_2$, $(Ph_4C_4)PdCl_2$, $(COD)PtCl_2$, $K[PtCl_3(C_2H_4)]H_2O$, $[Pt(C_2H_4)Cl_2]_2$, $(PhCN)_2PtCl_2$, $[(C_2H_4)_2RhCl]_2$, and

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1 Ru(COD)Cl₂ wherein COD stands for 1,5-cyclooctadiene and
Ph₄C₄ for tetraphenylcyclobutadiene. Palladium complexes
such as (PhCN)₂PdCl₂ and [(C₂H₄)PdCl₂]₂ are preferred as
the platinum group metal complex used in this invention.

5 Examples of the carbonium salt and oxonium
salt used in this invention include onium salts consist-
ing of combinations of the following cations and anions:

10 Cations: triphenylmethyl ion [(C₆H₅)₃C⁺],
 tropylium ion (C₇H₇⁺),
 acyl ion (RCO⁺),
 dialkoxycarbonium ion [RC(OR')(OR'')⁺],
 triethyloxonium ion [(C₂H₅)₃O⁺],

15 In the above formulas, R, R' and R'' represent
independently an organic group, and usually
alkyls, aryls or aralkyls, and R, R' and R''
may be the same or different.

20 Anions: BF₄⁻, AlCl₄⁻, FeCl₄⁻, SnCl₅⁻, PF₆⁻, PCl₆⁻,
 SbCl₆⁻, SbF₆⁻, ClO₄⁻, CF₃SO₃⁻, CF₃CO₂⁻.
 Preferable cations are triphenylmethyl ion and
 triethyloxonium ion, and preferable anions are
 BF₄⁻ and ClO₄⁻.

25 Parabenoquinone derivatives used in this
invention include, for example, 2,3-dicyano-5-chloro-
parabenoquinone, 2,3-dichloro-5,6-dicyanoparabenzo-
quinone, 2,3-dicyano-5-phenylsulphonylparabenzoquinone,
2,3-dicyano-5-chloro-6-phenylsulfonylparabenzoquinone,
and 2,3,5,6-tetracyanoparabenzoquinone. Preferable
parabenzoquinone derivatives are those having the first

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1 half wave reduction potential ($-E_{1/2}$) of less than
-0.2 V at 25°C as measured by saturated calomel
electrode using LiClO₄ as a supporting electrolyte in
acetonitrile. The most preferred parabenoquinone
5 derivative is 2,3-dichloro-5,6-dicyanoparabenoquinone.

Note: The first half wave reduction potential of
parabenoquinone derivatives is described in,
for example, The Chemistry of the Quinoid
Compounds, Part 2, John Wiley and Sons (1974),
10 p. 770.

As the organic solvents used in this invention,
any kind of organic solvent may be used, as far as the
solvent can dissolve the above-mentioned platinum group
metal complex, carbonium salt, oxonium salt or
15 parabenoquinone derivative.

As the solvent, there may be mentioned, for
example, aromatic hydrocarbons such as benzene,
toluene, xylene and the like; nitro compounds such as
nitromethane, nitroethane, nitrobenzene and the like;
20 nitrile compounds such as acetonitrile, benzonitrile,
and the like; ether compounds such as diethyl ether,
tetrahydrofuran, dioxane, anisole, and the like; lower
alcohols such as methanol, ethanol, propanol and the
like; halogeno compounds such as dichloromethane,
25 chloroform, chlorobenzene, methylene chloride,
trifluoroacetic acid, and the like; ester compounds
such as methyl acetate, ethyl acetate and the like;
ketone compounds such as acetophenone, acetone and

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1 the like; sulfoxide compounds such as dimethylsulfoxide
and the like; amide compounds such as N,N-dimethyl-
formamide and the like; and lower organic acids such
as acetic acid and the like; and anhydrides of lower
5 organic acids.

The form of the starting acetylene polymer used is not critical, though it may be any of the powder, film and fiber. The doping treatment is preferably conducted under an inert gas atmosphere, since
10 the acetylene polymer is unstable against oxygen. For instance, the doping is carried out by immersing the acetylene polymer in an organic solvent solution of a platinum group metal complex, a carbonium salt, an oxonium salt or a parabenoquinone derivative. The
15 concentration of the solution used for doping is decided depending upon the solubility of the dopant used because the solubility of the dopant is varied depending on the kind of the dopant used. However, there is seen the tendency that the higher the concentration used, the
20 larger the weight increase of the polymer doped in a short period of time becomes. The period of immersing acetylene polymer may be varied depending upon the concentration of the solution used and the temperature for the doping treatment. The immersion temperature
25 is not critical and the immersion treatment may be

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1 effected at any temperature at which the dopant does
not decompose and the solvent does not solidify.

Generally, the immersion is effected at 10° to 70°C.

The doped acetylene polymer thus prepared
5 is subjected to measurement of electrical conductivity
by a 4-probe method. The electrical conductivity of
the doped polymer varies depending on the kind of
dopant and the weight increase of the doped acetylene
polymer. The larger the weight increase of the doped
10 acetylene polymer, the greater the electrical conductivity
of the doped acetylene polymer becomes. Therefore,
therefore, the electrical conductivity of the doped
acetylene polymer can be adjusted by controlling
the weight increase of the doped acetylene polymer.

15 Furthermore, the doped acetylene polymer is
also handled preferably under an inert gas atmosphere,
since the obtained polymer is also unstable against
oxygen.

This invention is illustrated below referring
20 to Examples, which are not by way of limitation but by
way of illustration. The acetylene polymer used in
the Examples was prepared by the following method:

Preparation of acetylene polymer

In a 500-ml glass vessel was placed 1.7 ml of

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1 titanium tetrabutoxide under a nitrogen atmosphere and was
dissolved in 30 ml of toluene in the vessel. Thereto was
added 2.7 ml of triethylaluminium with stirring to effect
reaction. The vessel containing the reaction product
5 was mounted on a polymerization apparatus, and the
catalyst solution contained in the vessel was solidified
by liquid nitrogen in the vessel, after which the
nitrogen in the vessel was removed by a vacuum pump.
The temperature of the vessel was returned to room
10 temperature to vaporize the nitrogen dissolved in the
solution and then the solution was again solidified by
liquid nitrogen and evacuated. Thereafter, the vessel
was kept at a temperature of a dry ice-methanol mixture
and purified acetylene was introduced into the vessel
15 under reduced pressure from a gas holder in which the
acetylene was stored in the static state.

Polymerization occurred at once on the surface
of the solution and an acetylene polymer in the form of
a film was formed. Thirty minutes after the introduction
20 of acetylene, the vessel was taken out of the polymeriza-
tion apparatus and nitrogen gas was introduced into
the vessel. The catalyst solution was removed from
the vessel by means of a syringe, and thereafter the
polymer obtained was dried and washed thoroughly with de-
25 oxygenated toluene. The toluene was thereafter removed
by means of a syringe, and the contents of the vessel
were dried under vacuum to obtain an acetylene polymer
film.

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1 The electrical conductivity of this acetylene
polymer film as measured by a 4-probe method was 10^{-8}
 $\Omega^{-1} \cdot \text{cm}^{-1}$.

Example 1

5 An acetylene polymer film was immersed in a
solution of 0.2 g of $[(\text{C}_2\text{H}_4)\text{PdCl}_2]_2$ in 20 ml of dried
deoxygenated chloroform, and allowed to stand at room
temperature for 24 hrs. This acetylene polymer film
was thereafter transferred to another vessel, washed
10 with chloroform and vacuum-dried. The electrical
conductivity of the doped acetylene film thus obtained
was $3 \times 10^{-2} \Omega^{-1} \cdot \text{cm}^{-1}$ as measured by a 4-probe method.
The doped acetylene polymer in the form of a film was
subjected to the ESCA (electron spectroscopy for
15 chemical analysis) measurement to detect only divalent
Pd. From this fact, it was understood that the
electrical conductivity of the doped acetylene polymer
was increased as a result of the acetylene polymer
having been doped with the Pd compound and the Pd metal
20 deposited upon decomposition of the complex did not
participate in the increase in electrical conductivity.

When the doped acetylene polymer was allowed to
stand for 6 months at 100°C at a reduced pressure of 10^{-1}
Torr or under natural weather conditions in a glass
25 container at a reduced pressure of 10^{-1} Torr, substantially
no change in electrical conductivity was observed.

It is to be noted that, in this Example, all
the procedures were carried out under a nitrogen

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1 atmosphere so as not to expose the acetylene polymer to
air, and the same applies to the subsequent Examples
unless otherwise specified.

Example 2

5 An acetylene polymer film was immersed in a
solution of 0.1 g of $(\text{PhCN})_2\text{PdCl}_2$ in 20 ml of dried
deoxygenated methylene chloride and allowed to stand
at room temperature for 24 hrs. This acetylene polymer
film was then transferred to another vessel, washed with
10 fresh methylene chloride and vacuum-dried. The doped
acetylene polymer film thus obtained had an electrical
conductivity of $3 \times 10^{-3} \Omega^{-1} \cdot \text{cm}^{-1}$.

Example 3

An acetylene polymer film was immersed in a
15 solution of 0.1 g of $(\text{PhCN})_2\text{PtCl}_2$ in 20 ml of dried
deoxygenated methylene chloride and allowed to stand at
room temperature for 24 hrs. This acetylene polymer
film was then transferred to another vessel and washed
with fresh methylene chloride and vacuum-dried. The
20 electrical conductivity of the doped acetylene polymer
film thus obtained was $7 \times 10^{-5} \Omega^{-1} \cdot \text{cm}^{-1}$.

Example 4

An acetylene polymer film was immersed in a
solution of 0.1 g of $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$ in dried deoxygenated
25 methylene chloride and allowed to stand at room

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1 temperature for 24 hours. This acetylene polymer film
was thereafter transferred to another vessel, washed
with fresh methylene chloride and vacuum-dried.

The electrical conductivity of the doped
5 acetylene polymer film thus obtained was 5×10^{-5}
 $\Omega^{-1} \cdot \text{cm}^{-1}$.

Example 5

An acetylene polymer film was immersed in a
solution of 0.1 g of $\text{Ru}(\text{COD})\text{Cl}_2$ in 20 ml of dried
10 deoxygenated chloroform and allowed to stand at room
temperature for 24 hrs. This acetylene polymer film
was thereafter transferred to another vessel, washed
with fresh chloroform and vacuum-dried.

The doped acetylene polymer film thus
15 obtained had an electrical conductivity of 6×10^{-5}
 $\Omega^{-1} \cdot \text{cm}^{-1}$.

Example 6

An acetylene polymer film was immersed in a
dried methylene chloride solution of $(\text{C}_2\text{H}_5)_3\text{O}^+\text{BF}_4^-$
20 (0.3 g/10 ml), subjected to deaeration, and then allowed
to stand at room temperature for 24 hrs. This acetylene
polymer film was thereafter transferred to another
vessel, washed with fresh methylene chloride, and
vacuum-dried. All the procedures were carried out
25 under an argon atmosphere.

The doped acetylene polymer film thus obtained
had an electrical conductivity of $5 \times 10^{-2} \Omega^{-1} \cdot \text{cm}^{-1}$.

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- 1 When the doped acetylene polymer was allowed to stand for
6 months at 100°C at a reduced pressure of 10^{-1} Torr or
under natural weather conditions in a glass container at
a reduced pressure of 10^{-1} Torr, substantially no change
5 in electrical conductivity was observed.

Example 7

- An acetylene polymer film was immersed in a dried methylene chloride solution of $(C_6H_5)_3C^+BF_4^-$ (0.3 g/10 ml), subjected to deaeration, and allowed to 10 stand at room temperature for 24 hrs. This acetylene polymer film was thereafter transferred to another vessel, washed with fresh methylene chloride and dried under vacuum. The doped acetylene polymer film thus obtained had an electrical conductivity of $3 \times 10^{-1} \Omega^{-1} \cdot cm^{-1}$.
15 All the procedures were carried out under an argon atmosphere.

Example 8

- In 20 ml of dried deoxygenated benzene was dissolved 0.1 g of 2,3-dichloro-5,6-dicyanoparabeno-20 quinone ($-E_{1/2} = -0.5$ V). An acetylene polymer film was immersed in the solution, and allowed to stand at room temperature for 24 hrs. This acetylene polymer film was thereafter transferred to another vessel and vacuum-dried. The doped acetylene polymer film thus obtained had an 25 electrical conductivity of $2 \times 10^{-1} \Omega^{-1} \cdot cm^{-1}$.

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1 Example 9

In 20 ml of dried deoxygenated benzene was dissolved 0.1 g of 2,3-dicyano-5-chloroparabenoquinone ($-E_{1/2} = -0.41$ V). An acetylene polymer film was
5 immersed in the solution and allowed to stand at room temperature for 24 hrs. This acetylene polymer film was transferred to another vessel and vacuum-dried. The doped acetylene polymer film thus obtained had an electrical conductivity of $5 \times 10^{-3} \Omega^{-1} \cdot \text{cm}^{-1}$.

10 Example 10

An acetylene polymer film was immersed in a solution of 0.1 g of $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$ in 20 ml of dried deoxygenated acetone and allowed to stand at room temperature for 24 hrs. This acetylene polymer film was
15 thereafter transferred to another vessel, washed with fresh acetone and then dried under vacuum. The doped acetylene polymer film thus obtained had an electrical conductivity of $8 \times 10^{-5} \Omega^{-1} \cdot \text{cm}^{-1}$.

Example 11

20 An acetylene polymer film was immersed in a solution of 0.1 g of $(\text{COD})\text{PdCl}_2$ in 20 ml of dried deoxygenated methylene chloride, and allowed to stand at room temperature for 24 hrs. This acetylene polymer film was thereafter transferred to another vessel, washed
25 with fresh methylene chloride, and then dried under vacuum. The doped acetylene polymer film thus obtained

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1 had an electrical conductivity of $7 \times 10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$.

Example 12

An acetylene polymer film was immersed in a solution of 0.1 g of $(\text{COD})\text{PtCl}_2$ in 20 ml of dried deoxygenated fresh methylene chloride, and allowed to stand at room temperature for 24 hrs, after which the acetylene polymer film was taken out of the solution, washed with methylene chloride, and then dried under vacuum. The doped acetylene polymer film thus obtained had an electrical conductivity of $2 \times 10^{-5} \Omega^{-1} \cdot \text{cm}^{-1}$.

Example 13

An acetylene polymer film was immersed in a solution of 0.1 g of $(\text{Ph}_4\text{C}_4)\text{PdCl}_2$ in 20 ml of dried deoxygenated methylene chloride, and allowed to stand at room temperature for 24 hrs. This acetylene polymer film was thereafter transferred to another vessel, washed with fresh methylene chloride, and then dried under vacuum. The doped acetylene polymer film thus obtained had an electrical conductivity of $3 \times 10^{-5} \Omega^{-1} \cdot \text{cm}^{-1}$.

20 Example 14

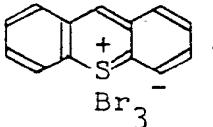
An acetylene polymer film was immersed in a solution of 0.2 g of $\text{p-ClC}_6\text{H}_4\text{N}_2\text{PF}_6$ in 20 ml of dried deoxygenated ethanol, and allowed to stand at room temperature for 24 hrs. This acetylene polymer film was thereafter transferred to another vessel, washed with fresh

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1 ethanol, and then dried under vacuum. The doped
acetylene polymer film thus obtained had an electrical
conductivity of $1 \times 10^{-4} \Omega^{-1} \cdot \text{cm}^{-1}$.

Example 15

5 An acetylene polymer film was immersed in a
solution of 0.1 g of $\text{C}_{13}\text{H}_9\text{SBr}_3$ in 20 ml of dried
deoxygenated methanol, and allowed to stand at room
temperature for 24 hrs. This acetylene polymer film was
thereafter transferred to another vessel, washed with
10 fresh methanol, and then dried under vacuum. The doped
acetylene polymer film thus obtained had an electrical
conductivity of $7 \times 10^{-5} \Omega^{-1} \cdot \text{cm}^{-1}$.

Said $\text{C}_{13}\text{H}_9\text{SBr}_3$ means thioxanthylium perbromide
having the structural formula, .

15 Example 16

An acetylene polymer film was immersed in a
solution of 0.1 g of $\text{Ph}_3\text{C}^+\text{ClO}_4^-$ in 20 ml of dried
deoxygenated methylene chloride, and allowed to stand at
room temperature for 24 hrs. This acetylene polymer
20 film was thereafter transferred to another vessel, washed
with fresh methylene chloride and then dried under
vacuum. The doped acetylene polymer thus obtained had
an electrical conductivity of $3 \times 10^1 \Omega^{-1} \cdot \text{cm}^{-1}$.

Example 17

25 Triphenylmethyl trifluoroacetate was

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- 1 synthesized by adding 0.5 g of Ph_3COH to 3 ml of dried deoxygenated trifluoroacetic acid, and in the resulting reaction mixture was immersed an acetylene polymer film, and allowed to stand at room temperature for 24 hrs.
- 5 This acetylene polymer film was thereafter transferred to another vessel, washed with fresh trifluoroacetic acid and then dried under vacuum. The doped acetylene polymer film thus obtained had an electrical conductivity of $3 \times 10^{-4} \Omega^{-1} \cdot \text{cm}^{-1}$.
- 10 For comparison, an acetylene polymer film was immersed in 3 ml of deoxygenated trifluoroacetic acid and allowed to stand at room temperature for 24 hrs. The acetylene polymer film was thereafter taken out of the trifluoroacetic acid, and then dried under vacuum.
- 15 The acetylene polymer film thus treated had an electrical conductivity of less than $10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$.

Example 18

- An acetylene polymer film was immersed in a solution of 0.1 g of $\text{C}_{13}\text{H}_9\text{SI}_5$ in 20 ml of dried deoxygenated methanol and allowed to stand at room temperature for 24 hrs. This acetylene polymer film was thereafter transferred to another vessel, washed with fresh methanol and then dried under vacuum. The doped acetylene polymer film had an electrical conductivity of $8 \times 10^{-4} \Omega^{-1} \cdot \text{cm}^{-1}$.

Said $\text{C}_{13}\text{H}_9\text{SI}_5$ means thioxanthylium periodide having the structural formula,

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WHAT IS CLAIMED IS:

1. An acetylene polymer doped with a dopant selected from the group consisting of a platinum group metal complex, a carbonium salt, an oxonium salt and a parabenoquinone derivative.
2. A doped acetylene polymer according to claim 1, wherein the dopant is a platinum group metal complex selected from the group consisting of $(\text{PhCN})_2\text{PdCl}_4$, $(\text{COD})\text{PdCl}_2$, $[(\text{C}_2\text{H}_4)\text{PdCl}_2]_2$, $(\text{Ph}_4\text{C}_4)\text{PdCl}_2$, $(\text{COD})\text{PtCl}_2$, $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]\text{H}_2\text{O}$, $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$, $(\text{PhCN})_2\text{PtCl}_2$, $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$ and $\text{Ru}(\text{COD})\text{Cl}_2$ wherein COD stands for 1,5-cyclooctadiene and Ph_4C_4 for tetraphenylcyclobutadiene.
3. A doped acetylene polymer according to claim 1, wherein the dopant is a palladium complex.
4. A doped acetylene polymer according to claim 3, wherein the dopant is $(\text{PhCN})_2\text{PdCl}_2$ or $[(\text{C}_2\text{H}_4)\text{PdCl}_2]_2$.
5. A doped acetylene polymer according to claim 1, wherein the dopant is a combination of an anion selected from the group consisting of BF_4^- , AlCl_4^- , FeCl_4^- , SnCl_5^- , PF_6^- , PCl_6^- , SbCl_6^- , SbF_6^- , ClO_4^- , CF_3SO_3^- and CF_3CO_2^- with a cation selected from the group consisting of triphenylmethyl ion $[(\text{C}_6\text{H}_5)_3\text{C}^+]$, tropylium ion (C_7H_7^+) , acyl ion (RCO^+) , triethyloxonium ion $[(\text{C}_2\text{H}_5)_3\text{O}^+]$, and dialkoxycarbonium ion $[\text{RC}(\text{OR}')(\text{OR}'')^+]$ in which R, R' and R'' stand for organic groups.
6. A doped acetylene polymer according to claim 1, wherein the dopant is a combination of an anion selected from the group consisting of BF_4^- and ClO_4^- with a cation

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selected from the group consisting of triphenylmethyl ion $[(C_6H_5)_3C^+]$ and triethyloxonium ion $[(C_2H_5)_3O^+]$.

7. A doped acetylene polymer according to claim 1, wherein the dopant is a parabenoquinone derivative selected from the group consisting of 2,3-dicyano-5-chloroparabenoquinone, 2,3-dichlorodicyanoparabenoquinone, 2,3-dicyano-5-phenylsulfonylparabenoquinone, 2,3-dicyano-5-chloro-6-phenylparabenoquinone and 2,3,5,6-tetracyanoparabenoquinone.
- 10 8. A doped acetylene polymer according to claim 7, wherein the parabenoquinone derivative has a first half wave reduction potential ($-E_{1/2}$) of less than -0.2 V as measured at 25°C by means of a saturated calomel electrode using $LiClO_4$ in acetonitrile as the supporting electrolyte.
- 15 9. A doped acetylene polymer according to any one of claims 1 to 8, wherein the starting acetylene polymer is in the form of film.
- 10 10. A process for producing a doped acetylene polymer which comprises immersing an acetylene polymer under an inert gas atmosphere in an organic solvent solution of a dopant selected from the group consisting of a platinum group metal complex, a carbonium salt, an oxonium salt and a parabenoquinone derivative.
- 20 11. A process according to claim 10, wherein the immersion is carried out at 10° to 70°C.
- 25 12. A process according to claim 10, wherein the

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- dopant is a platinum group metal complex selected from the group consisting of $(\text{PhCN})_2\text{PdCl}_2$, $(\text{COD})\text{PdCl}_2$, $[(\text{C}_2\text{H}_4)\text{PdCl}_2]_2$, $(\text{Ph}_4\text{C}_4)\text{PdCl}_2$, $(\text{COD})\text{PtCl}_2$, $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]\text{-H}_2\text{O}$, $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$, $(\text{PhCN})_2\text{PtCl}_2$, $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$, and 5 $\text{Ru}(\text{COD})\text{Cl}_2$, wherein COD stands for 1,5-cyclooctadiene and Ph_4C_4 for tetraphenylcyclobutadiene.
13. A process according to claim 10, wherein the dopant is a palladium complex.
14. A process according to claim 13, wherein the 10 palladium complex is $(\text{PhCN})_2\text{PdCl}_2$ or $[(\text{C}_2\text{H}_4)\text{PdCl}_2]_2$.
15. A process according to claim 10, wherein the dopant is a combination of a cation selected from the group consisting of triphenylmethyl ion $[(\text{C}_6\text{H}_5)_3\text{C}^+]$, tropylium ion $(\text{C}_7\text{H}_7)^+$, acyl ion $(\text{RCO})^+$, dialkoxycarbonium ion $[\text{RC}(\text{OR}')_2]^+$, and triethyloxonium ion $[(\text{C}_2\text{H}_5)_3\text{O}]^+$ with an anion selected from the group consisting of BF_4^- , 15 AlCl_4^- , FeCl_4^- , SnCl_5^- , PF_6^- , PCl_6^- , SbCl_6^- , SbF_6^- , ClO_4^- , CF_3SO_3^- and CF_3CO_2^- .
16. A process according to claim 10, wherein the 20 dopant is a parabenoquinone derivative selected from the group consisting of 2,3-dicyano-5-chloroparabenoquinone, 2,3-dichloro-5,6-dicyanoparabenoquinone, 2,3-dicyano-5-phenylsulfonylparabenoquinone, 2,3-dicyano-5-chloro-6-phenylsulfonylparabenoquinone and 2,3,5,6-tetracyanopara-25 benzoquinone.

17. A process according to claim 16, wherein the parabenoquinone derivative has a first half wave reduction potential ($-\text{E}_{1/2}$) of less than -0.2 V as measured

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at 25°C by means of a saturated calomel electrode using LiClO₄ as a supporting electrolyte in acetonitrile.

18. A process according to claim 10, wherein the organic solvent is selected from the group consisting
5 of aromatic hydrocarbons, nitrile compounds, nitro compounds, ether compounds, lower alcohols, halogeno compounds, ester compounds, ketone compounds, sulfoxide compounds and lower organic acids and their anhydrides.

19. A process according to claim 10, wherein
10 the organic solvent is a compound selected from the group consisting of benzene, toluene, xylene, nitromethane, nitroethane, nitrobenzene, acetonitrile, benzonitrile, diethyl ether, tetrahydrofuran, dioxane, anisole, methanol, ethanol, propanol, dichloromethane,
15 chloroform, chlorobenzene, methylene chloride, trifluoroacetic acid, methyl acetate, ethyl acetate, acetone, acetophenone, dimethylsulfoxide, N,N-dimethyl-formamide, acetic acid and acetic anhydride.



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EUROPEAN SEARCH REPORT

0022271

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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.)
Category	Citation of document with indication, where appropriate of relevant passages	Relevant to claim	
A	US - A - 3 926 907 (ENGLE) + Columns 8,9 + --		C 08 L 49/00 C 08 J 3/20// C 08 K 3/10 C 08 K 5/08 C 08 K 5/09 H 01 B 1/00
A	US - A - 2 351 108 (COLLINS) -----		TECHNICAL FIELDS SEARCHED (Int.Cl.)
			C 08 L C 08 J C 08 K H 01 B
			CATEGORY OF CITED DOCUMENTS
X	<p>The present search report has been drawn up for all claims</p> <p>X member of the same patent family, corresponding document</p>		
Date of search	Date of completion of the search	Examiner	
VIENNA	10-10-1980	DICHER	